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(54) TRANSPARENT CONDUCTIVE FILM AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a transparent conductive film and a method for producing it in which the transparent conductive film having a metallic layer with a formed minute pattern and equipping both high transparency and electrical conductivity is easily produced at a low cost without necessitating a complex process.

SOLUTION: The transparent conductive film has both a film formed into a prescribed pattern by exposure through the photomask of photosensitive material containing an electroless plating catalyst and a patternlike metallic layer formed into a film by electroless plating on the above-mentioned film. The transparent conductive film is constituted so as to form the patternlike metallic layer formed into the film by applying photosensitive material containing the electroless plating catalyst on the surface of a transparent substrate and drying it and performing exposure through the photomask and performing development to form a patterned film and then performing electroless plating treatment.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the transparence electric conduction film which has high transparency and conductivity useful as the transparent electrode of the leakage electromagnetic wave screen of various indicating equipments, and various electron devices, a transparence planar heating element, etc., and its manufacture approach.

[0002]

[Description of the Prior Art] The thing which formed conductive ingredients, such as what stuck a conductive mesh on the transparence electric conduction film conventionally used as the transparent electrode of the leakage electromagnetic wave screen of various indicating equipments, such as CRT, PDP, and a liquid crystal display, and various electron devices, or a transparence planar heating element at the transparence base, a metal, and ITO, on the transparence base by vacuum evaporation or sputtering, and publication number 5 No. -16281 official report, publication number 5-283889 There was transparence electric conduction film which is indicated by the number official report.

[0003] The outline of the transparence electric conduction film indicated by these official reports is the following, and is made and manufactured.

** Form a hydrophilic transparence resin layer on a transparence base, and make a plating catalyst adsorb.

** Form an electroless deposition layer on a hydrophilic transparence resin layer.

** Make a hydrophilic transparence resin layer black.

** Form the pattern-like resist section on an electroless deposition layer.

** Etching removes the non-resist section and form the patternized transparence electric conduction film.

[0004] [Trouble] There were various troubles as shown below by said conventional transparence electric conduction film. When a conductive mesh is stuck on a transparence base, a metal mesh and the mesh which plated the front face of fiber with the metal are used. Since that in which specification became settled was used, it was difficult for each mesh to change the line breadth and the pitch of a mesh freely, and it was what has a limitation in making line breadth small especially, and is inferior to visibility. Moreover, in order to raise visibility, when a mesh front face tends to be black-ized and it is going to suppress reflection of a mesh front face, a process becomes complicated and cost becomes high.

[0005] If thickness is thickened in order that visibility may acquire bad and sufficient conductivity for metallic luster when conductive ingredients, such as a metal and ITO, are formed on a transparence base by vacuum evaporation or sputtering, since light will be absorbed, permeability worsens remarkably. Moreover, by the film of transparent conductive ingredients, such as ITO, conductivity is low, and an application is limited, and it is expensive.

[0006] In the case of the transparence electric conduction film given in an official report, since a hydrophilic transparence resin layer is formed on a transparence base and it is manufactured, a production process becomes complicated and becomes in cost and expensive. Moreover, whenever

[black] is not enough, and when strabism of the transparence electric conduction film is carried out, a metallic luster color is conspicuous [there is reflection by the metal particle, and], although the black-ized hydrophilic resin layer is shaded by the detailed metal particles which deposited at the time of electroless deposition.

[0007]

[Problem(s) to be Solved by the Invention] This invention is to offer the transparence electric conduction film to which a complicated process was not needed, but it is easy for and the transparence electric conduction film which it was, and the technical problem for it has the metal layer in which the detailed pattern was formed, and has high transparency and conductivity was made to be made as for manufacture cheaply and its manufacture approach for canceling said trouble in a Prior art.

[0008]

[Means for Solving the Problem] The transparence electric conduction film concerning claim 1 in this invention is characterized by having the coat formed in the predetermined pattern of exposure through the photo mask of the photosensitive ingredient containing an electroless deposition catalyst, and the pattern-like metal layer formed by electroless deposition on this coat.

[0009] The transparence electric conduction film concerning claim 2 is characterized by said predetermined pattern having the shape of the shape of a grid, and a mesh.

[0010] The numerical aperture of said pattern-like metal layer the transparence electric conduction film concerning claim 3 It is characterized by being more than 50 %.

[0011] The transparence electric conduction film concerning claim 4 is characterized by said pattern-like metal layers being copper, nickel, silver, gold, platinum, palladium, two or more sorts of those combination, or an alloy.

[0012] The transparence electric conduction film concerning claim 5 is characterized by said electroless deposition catalyst being a colloid metal particle.

[0013] The transparence electric conduction film concerning claim 6 is characterized by said electroless deposition catalyst being a metal salt or a metal complex.

[0014] The transparence electric conduction film concerning claim 7 is characterized by the sensitive material containing said electroless deposition catalyst being a thing containing a black pigment.

[0015] Moreover, the manufacture approach of the transparence electric conduction film concerning claim 8 is characterized by applying the sensitive material containing an electroless deposition catalyst on the front face of a transparence base, drying, forming the coat which is exposed, develops negatives through a photo mask and has a predetermined pattern, and making the pattern-like metal layer subsequently formed by performing electroless deposition processing form.

[0016]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained concretely. However, the gestalt of this operation is concretely explained in order to make the meaning of invention understand better, and especially, as long as there is no assignment, it does not limit the contents of invention.

[0017] [Transparence electric conduction film] The transparence electric conduction film formed has the coat which formed the detailed predetermined pattern by exposure through the photo mask of the photosensitive ingredient containing an electroless deposition catalyst, and the pattern-like metal layer formed by electroless deposition on this coat.

[0018] This transparence electric conduction film applies and dries the photosensitive ingredient containing an electroless deposition catalyst on a transparence base, exposes and develops a photosensitive ingredient by wave energies, such as ultraviolet rays, through a photo mask, forms the coat which has the predetermined pattern of a detailed pattern, and forms the pattern-like metal layer formed by performing electroless deposition processing on that coat. It is desirable to be able to form the shape of the shape of a grid and a mesh, in the shape of a stripe, etc., and to form the shape of a grid and in the shape of a mesh especially as a predetermined pattern.

[0019] Let especially pattern-like metal layers be copper, nickel, silver, gold, platinum, palladium, those two or more sorts of combination, or an alloy. And let an electroless deposition catalyst be the metaled

metal salt or metaled metal complex which has an electroless deposition catalysis to the metal which forms the metaled colloid particle which has an electroless deposition catalysis to the metal which forms said pattern-like metal layer, or said metal, or said pattern-like metal layer, or said metal.

[0020] [Colloid particle] The colloid particle of the metal which can be used will not be limited especially if it is the metaled colloid particle which has an electroless deposition catalysis to the metal or said metal of what shows autocatalysis, i.e., said pattern-like metal layer, at the time of electroless deposition processing.

[0021] When using palladium, it is easily obtained by returning palladium compounds, such as a palladium chloride, with reducing agents, such as sodium borohydride, to the bottom of existence of surfactants, such as protective colloid like a polyvinyl pyrrolidone or sodium dodecylbenzenesulfonate.

[0022] [A fusibility metal salt or metal complex] The fusibility metal salt or metal complex which can be used will not be limited especially if it is the metaled metal salt or metaled metal complex which has an electroless deposition catalysis to the metal or said metal of what shows autocatalysis, i.e., said pattern-like metal layer, at the time of electroless deposition processing.

[0023] When using a water-soluble photosensitive ingredient, copper, nickel, silver, gold, platinum, the nitrate of palladium, a sulfate, a chloride, etc. can use the metal salt of the water solubility generally known. When using a meltable photosensitive ingredient for a solvent, organometallic complexes, such as acetate of copper, nickel, silver, gold, platinum, and palladium, can be used. It exists as a big and rough particle within the coat pattern after hardening, and the uniform plating film is not obtained at the time of electroless deposition processing, and since it becomes the cause of a pattern configuration and a conductive defect, what is not dissolved in the dilution solvent of a photosensitive ingredient is not used.

[0024] [Photosensitive ingredient] As a photosensitive ingredient, the photoresist of the positive type generally marketed or a negative mold can be used. Moreover, even if it uses the thing which mixed the photoresist to organic and inorganic a filler and a polymer, and gave photosensitivity to them, or the ingredient from which solubility changes with the exposure like an organometallic compound to a developer, it does not interfere.

[0025] [Addition of the electroless deposition catalyst to a photosensitive ingredient] Consideration suitable for those ingredients is required for addition of the electroless deposition catalyst to a photosensitive ingredient at a metal colloid particle and the case where a fusibility metal salt or a metal complex is made to contain.

[0026] in order to make a photosensitive ingredient contain a metal colloid particle and to avoid condensation of a metal particle -- a surfactant like protective colloid like a polyvinyl pyrrolidone or vinyl alcohol, or sodium dodecylbenzenesulfonate -- a metal -- receiving -- 0.05-50 a weight % grade -- mixing beforehand is desirable.

[0027] In order to make a photosensitive ingredient contain a fusibility metal salt or a metal complex, it is desirable to mix it generally, after this metal salt or a metal complex dissolves in a dilution solvent beforehand since solubility is not so large. Thereby, generating of the defect of the plating film by the big and rough particle can be prevented.

[0028] [Exposure processing] The photosensitive ingredient containing the electroless deposition catalyst acquired by doing in this way is applied and dried to homogeneity on a transparence substrate by print processes, such as the applying methods, such as a spin coat, a roll coat, and a flow coat, or screen-stencil, and flexographic printing. As an approach of processing this catalyst content photosensitivity ingredient into the coat which has a predetermined pattern, it exposes through a photo mask. When the photosensitive ingredient to be used is a positive type, the photo mask of the same pattern as a predetermined pattern coat is used, and, in the case of a negative mold, the photo mask which reversed a part for white Kurobe to the positive pattern should just be used. In order to harness the advantage of the patternizing by exposure at this time, it is the line breadth of a pattern coat. 40 Carrying out to below μm is desirable. Furthermore, line breadth 20 By carrying out to below μm grade, recognition of the pattern section by viewing is possible also for the difficult thing visually acquired for the uniform electric conduction film.

[0029] The wavelength and exposure energy of light to irradiate are suitably decided according to the photolysis or photo-curing property of the photosensitive ingredient to be used, and especially if patternizing is possible, they will not be limited by development. In the case of removal of an exposure part, and a negative-mold photosensitivity ingredient, development carries out using the developer from which a part for an unexposed part is removable, and makes a pattern coat form with a positive type photosensitivity ingredient. Then, heating or exposure is performed if needed, hardening of a pattern coat is promoted, and it considers as a predetermined resist pattern.

[0030] [Electroless deposition processing] It is immersed in the electroless deposition liquid of the metal which is going to obtain the base which gave the predetermined resist pattern, and a metal membrane is alternatively formed on a resist pattern. The thing of marketing which consists of water solutions, such as pH regulators, such as reducing agents, such as water-soluble metal salts, such as copper, nickel, silver, gold, platinum, a sulfate of each ** plated metal of palladium, and a hydrochloride, hypophosphorous acid and sodium borohydride, a hydrazine, and formalin, an inorganic acid, and an organic acid, and a complexing agent, a stabilizer, and a surfactant, can be used for electroless deposition liquid.

[0031] [Other additives] In order to stop the reflection factor of the reflected light produced in the interface of a resist pattern and a base, a black pigment can be added into a photosensitive ingredient if needed. A black pigment can use the mixture of black inorganic pigments, such as carbon black, graphite, low hypo---ic acid-ized titanium, and copper oxide-chrome oxide, or the organic pigment which shows black. Moreover, a mat agent can also be added. As an inorganic mat agent, minute beads, such as polystyrene resin and acrylic resin, can be used as particles, such as colloidal silica and a zinc oxide, and an organic mat agent.

[0032] [Other coatings] In addition to this according to the function for which the transparence base is asked, coatings, such as under coats, such as a primer for resistance grant of permselective membrane, such as an antireflection film, a glare-proof layer, antistatic film, pollution-control film, ultraviolet-rays electric shielding, and heat ray electric shielding, and a metal pattern, or a rebound ace court, can be performed.

[0033] in this way, if obtained, the transparence electric conduction film and the light permeability more than 50 % will be obtained easily -- the low resistance below 100ohm/** can be acquired easily. moreover, the electric conduction pattern section 20 by considering as the line breadth below mum grade, recognition of the pattern by viewing is difficult -- it can consider as the uniform electric conduction film visually.

[0034]

[Example] [the 1st example] -- pure water 2000 the palladium-chloride (Kanto chemistry company make) 2 weight section and the commercial hydrochloric-acid 3 weight section are added to the weight section -- heating stirring was carried out and it dissolved in 60 **. To this palladium-chloride water solution, it is polyvinyl alcohol **500 10 (the Kanto chemistry company make). It is pure water about the weight section. 2000 The protective colloid water solution which dissolved in the weight section was added. next, this solution while carrying out heating stirring at 40 ** -- the sodium-borohydride (Kanto chemistry company make) 1 weight section -- pure water 2000 the reducing-agent solution which dissolved in the weight section is added -- 30 It stirred between parts and cooled radiationally to the room temperature.

[0035] It is to this solution. 10 % polyvinyl alcohol **500 After adding the water-solution (Kanto chemistry company make) 200 weight section, evaporation removal of the pure water is carried out using a rotary evaporator, and it is all volume. 50 It considered as the palladium colloid water dispersion (palladium concentration abbreviation 2.4%) of the weight section.

[0036] Palladium colloid water dispersion 15 The weight section and pure water 40 SPP-LS -400 (Oriental composition industrial company make; solid content 13.18%) which is the still BAZORU conversion PVA which is a water-soluble negative-mold photoresist at the solution which mixed the weight section to homogeneity 30 The weight section is mixed and it is 2-n-butoxy ethanol under stirring. The resist coating liquid which adds 12 weight section and the 2-propanol-3 weight section, and

contains a fusibility metal salt was adjusted.

[0037] It is thickness about this coating liquid. It is thickness on the base made of acrylic resin of 2mm and 100mm angles. 0.08 Spin coating was carried out so that it might be set to μm . With and 70 ** 10 Rhine/tooth space after drying between parts = 10 μm / 90 The photo mask of μm is minded. 20 mJ/cm^2 Ultraviolet-rays exposure was carried out on exposure conditions. Next, negatives were developed by being immersed in the pure water of 40 ** for 2 minutes, and after that, the shower rinse was carried out with pure water, and the resist for an unexposed part was removed completely.

[0038] Non-electrolytic copper plating was performed to the acrylic resin plate with which the resist pattern of the shape of this grid was formed, and metal copper was alternatively deposited on the resist pattern to it. Thus, surface-electrical-resistance value of the obtained transparence electric conduction film 0.5ohm/**, and light permeability were 72%, and it was [rather than it was easy] the uniform film substantially to recognize the grid pattern of a current carrying part in viewing.

[0039] The [2nd example] OFPR-800 which is a positive type photoresist (TOKYO OHKA KOGYO CO., LTD. make) 20 Acetic-acid ethylcellosolve which dissolved the acetic-acid palladium 1 weight section in the weight section beforehand at homogeneity (Wako Pure Chem industrial company make) The resist coating liquid which mixes the 200 weight sections and contains a fusibility metal complex was adjusted.

[0040] It is thickness about this coating liquid. It is thickness on the soda lime glass of 3mm and 150 mm angles. 1.00 Spin coating was carried out so that it might be set to μm . 80 With ** 20 Rhine / tooth-space = 5micrometer / 95 after drying between parts The photo mask of μm is minded. 15 mJ/cm^2 Ultraviolet-rays exposure was carried out on exposure conditions. 40 In the NMD-3 phenomenon liquid of ** (TOKYO OHKA KOGYO CO., LTD. make) 90 Negatives were developed by being immersed between parts, and after that, the shower rinse was carried out with pure water, and the resist of an exposure part was removed completely.

[0041] Electroless nickel plating was performed to the glass plate with which the resist pattern of the shape of this grid was formed, and metal nickel was alternatively deposited on the resist pattern in it. Thus, surface-electrical-resistance value of the obtained transparence electric conduction film 3.0ohm/**, and light permeability It was 80 %, and it was [rather than it was easy] the uniform film substantially to recognize the grid pattern of a current carrying part in viewing.

[0042] As an example of a comparison, the ITO spatter film and the surface-electrical-resistance value of a conductive mesh, light permeability, and Rhine/tooth space are shown below.

[0043]

[Table 1]

| | 実施例 1 | 実施例 2 | 比較例 1 | 比較例 2 |
|-------------------------------|---------|--------|-------|----------|
| 表面抵抗値 (Ω/\square) | 0.5 | 3.0 | 100 | 0.1 |
| 可視光透過率 (%) | 72 | 80 | 85 | 50 |
| ライン/スペース (μm) | 10 / 90 | 5 / 95 | 均一膜 | 50 / 450 |

[0044]

[Effect of the Invention] By the transparence electric conduction film applied to claim 1 by this invention as mentioned above The coat formed in the predetermined pattern of exposure through the photo mask of the photosensitive ingredient containing an electroless deposition catalyst, Since it has the

pattern-like metal layer formed by electroless deposition on this coat A pattern-like metal layer can be formed on the electroless deposition catalyst which has a pattern more detailed than the conventional transperence electric conduction film which formed the hydrophilic transperence resin layer as a substrate, and the coat which has high conductivity and transparency can be obtained cheaply.

[0045] By the transperence electric conduction film concerning claim 2, the optimal transparency and conductivity can be easily adjusted by having made said predetermined pattern into the shape of the shape of a grid, and a mesh.

[0046] By the transperence electric conduction film concerning claim 3, the numerical aperture of said pattern-like metal layer Since it is more than 50 %, it can be made the need and sufficient transparency can be secured.

[0047] Since said pattern-like metal layers are copper, nickel, silver, gold, platinum, palladium, two or more sorts of those combination, or an alloy, electroless deposition can be possible and a metallic film can be made to form easily on the patternized electroless deposition catalyst by the transperence electric conduction film concerning claim 4.

[0048] Since said electroless deposition catalyst is a colloid metal particle, a photosensitive ingredient can be distributed easily that it is easy to treat, and the electroless deposition catalyst bed of a minute pattern can be made to form by the transperence electric conduction film concerning claim 5.

[0049] Even if it adds neither protective colloid nor a surfactant, the good dispersibility over a photosensitive ingredient is acquired and the electroless deposition catalyst bed of a minute pattern can be made to form by the transperence electric conduction film concerning claim 6, since said electroless deposition catalyst is a metal salt or a metal complex.

[0050] Since the photosensitive ingredient containing said electroless deposition catalyst contains a black pigment, while it suppresses the metallic luster of a plating coat and prevents reflection of the rear face of a transperence base, color nonuniformity and a metal color can be made to control by the transperence electric conduction film concerning claim 7.

[0051] By the manufacture approach of the transperence electric conduction film concerning claim 8, the sensitive material containing an electroless deposition catalyst is applied on the front face of a transperence base, it dries, and the coat which is exposed, develops negatives through a photo mask and has a predetermined pattern is formed. Subsequently By making the pattern-like metal layer formed by performing electroless deposition processing form The process which carries out adsorption support of the electroless deposition catalyst, and the process which carries out etching removal of the black pattern section under the electroless deposition layer of the non-resist section and this deposit become unnecessary at a hydrophilic transperence resin layer. A routing counter becomes less than the conventional approach, a production process can be simplified, a pattern-like metal layer can form membranes easily, and cost can be reduced.

[Translation done.]